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How accurate must a reference material be?

Abstract This article deals with reference materials (RMs) used for calibration purposes. For most common spectroscopic and chromatographic methods, RMs which have a relative content uncertainty of up to 3% can be used without considerably increasing the overall measurement uncertainty of the complete procedure. It is vital that the correct amount of the RM is used to ensure the quality of the quantitative chemical analyses. This can only be guaranteed if, in addition to the correct determination of the amount, the stability of the RM in the sales packaging is considered in the quoted uncertainty. For instance when the RM is packed in a container made of polyvinylidene fluoride water losses in hot climates can result in an increase in concentration which cannot be neglected. This is also true for high density polyethylene containers (PE-HD) although to a lesser degree. When mercury solutions of 1000 mg/l to 10 000 mg/l are kept in diluted nitric acid in PE containers, a relevant reduction in amount can be measured despite the water losses. However, the solutions remain stable in glass containers.

Key words Reference material · Stability · Calibration · Content uncertainty · Packaging

Introduction

This article deals with the specifications that must be met in connection with the uncertainty of the specified analyte content of reference materials (RMs) to permit them to be used as calibration substances for routine analytical work. In this case we need to differentiate between RMs for calibration and those for validation procedures.

While most RMs used for calibration consist of pure substances or their solutions, RMs used for validation are so-called matrix RMs which correspond to a real sample whose analytical content has usually been determined in an inter-laboratory comparison. This article deals exclusively with RMs used for calibration purposes. Both certified reference materials (CRMs) and uncertified RMs (RMs without a certificate according to ISO) are included. The main emphasis is put on metal ion solutions for atomic spectroscopy.

In analytical chemistry there are only a few absolute methods such as gravimetric and coulometric analysis. Most instruments used for quantitative chemical analysis have to be regularly calibrated with reference substances. The accuracy of the results depends on the quality of these substances. According to the EN 45001 standard, whenever possible, CRMs (CRM according to ISO Guides 31, 34 and 35) should be used for the calibration procedure. It is also possible to operate with less expensive uncertified stock solutions which can be traced to CRMs which can be subsequently used as reference substances. This means that, bearing in mind measurement uncertainty, the contents of the stock solution are determined with the aid of CRMs which are traced to the SI. Such stock solutions can themselves be produced, for instance from pure salts, or they can be purchased from manufacturers (so-called standard solutions). When using commercially available standard solutions, the contents must be traced to a CRM even though the manufacturer quotes these contents. This is not necessary when the manufacturer can prove that traceability to the SI has already been established.

Uncertainty of RMs used for calibration

A RM can be used for calibrating a procedure when the uncertainty of its analyte content (amount of substance) does not greatly affect the combined standard uncertainty of the complete analysis procedure. Staats and Noack [1] have made a proposal for grading the quality of matrix RMs. According to their findings, a

RM is usable when its contribution to the total uncertainty is not more than 5%. A good RM has a maximum impact of 2%, while 1% can be designated as very good. Due to a lack of information to the contrary, the authors classify the repeatability of the procedure as total uncertainty and base this on the fact that the total uncertainty can never be better than the repeatability. Because the combined standard uncertainty of a procedure is often greater than the repeatability, the grading of Staats and Noack is rather strict.

In the following sections we shall try to assess the influence produced by the uncertainty of RMs used for calibration on the combined standard uncertainty of normal analytical procedures, and thus introduce the definition of specifications. Depending on the particular problems defined by the sample, the analytical procedure and the analyte, the combined standard uncertainty can differ considerably. We shall concentrate on procedures employed in standard laboratories.

How large is the combined standard uncertainty of such procedures? Our experience in the analysis of technical products [2] shows that in most cases spectroscopic and chromatographic procedures achieve a relative combined standard uncertainty of 7% to 15%. To achieve a result under 5% demands a large increase in outlay which most clients are not prepared to pay. While the situation in the analysis of food products may be very similar, the relative uncertainties in environmental analysis are, for obvious reasons, often much higher than 20%. RMs suitable for analytical procedures which have a relative combined uncertainty of 5% should also be adequate for most normal procedures used in analytical chemistry. If in the first approximation we equate the reproducibility standard deviation s_R from an inter-laboratory comparison with the combined standard uncertainty, it turns out that our experience matches well with the results from inter-laboratory comparisons; using spectroscopic and chromatographic methods the relative reproducibility standard deviations are usually higher than 5%. An exception is found in titrimetric analyses and other analyses in which multi-stage sample preparation is not necessary, for example in some methods of water analysis.

The relative combined standard uncertainty $u_{c,rel}$ can be expressed as

$$u_{c,rel} = \sqrt{u_{c,rel}^0{}^2 + u_{RM,rel}^2}$$

where $u_{RM,rel}$ is the relative uncertainty of the used RM and $u_{c,rel}^0$ is the relative standard uncertainty of the procedure without any influence of the RM. When applied strictly, this equation is only valid

Table 1 Influence of reference materials (RMs) upon the combined standard uncertainty: $u_{c,rel}$ relative combined standard uncertainty, $u_{RM,rel}$ relative content uncertainty of RM

Increase of $u_{c,rel}$ by $u_{RM,rel}$	$u_{c,rel}$	$u_{RM,rel}$
0%	5%	0%
0.1%	5.005%	0.22%
1%	5.05%	0.7%
2%	5.1%	1.0%
5%	5.25%	1.6%
10%	5.5%	2.3%
20%	6.0%	3.3%
50%	7.5%	5.6%
100%	10%	8.7%

when a single RM is used for calibration and the content of this RM is fed into the equation as a factor for calculating the measured quantity. In our particular case we consider the above-mentioned equation as a schematic approximation which is more or less applicable for all relative analytical methods.

On the basis of this equation, a calculation is made for the impact of uncertainty of RMs on the relative combined standard uncertainty of an analytical procedure when $u_{c,rel}^0 = 5\%$ (see Table 1). For normal chromatographic methods and atomic spectroscopy such as gas chromatography (GC), high performance liquid chromatography (HPLC), ion chromatography (IC), atomic absorption spectroscopy (AAS) or atomic emission spectroscopy (AES), RMs with a relative uncertainty of up to 3% do not substantially affect the uncertainty of the overall procedure. Their impact on $u_{c,rel}$ remains below 20% and is therefore within the uncertainty of uncertainty estimates for chemical analytical procedures. If the homogeneity and preparation of the analytical sample do not have a large impact on the uncertainty of the procedure, which can be so in individual cases, for instance in water or drink analysis, a RM may be necessary which has a relative uncertainty of not more than 2%. Titrimetric analysis is an exception. Due to the high accuracy of individual titration methods a relative uncertainty of a maximum of 0.2–0.3% is often necessary for standard titration substances. On the other hand in environmental and trace analysis relative uncertainties of RMs up to 10 or 20% are often not to be found under the largest contributions to total uncertainty. Laboratories do not rely a priori on small uncertainties. RMs quoting the correct contents and uncertainty are more important. In this way the RMs can be selected according to the aims of the analytical task and their uncertainty calculated correctly within the overall uncertainty of the procedure.

Even when the content of a RM and its uncertainty has been reliably determined, the RM is only acceptable if its stability can be guaranteed through to the expiry date. A change in content can for instance be caused by the volatility of solvents, microbiological decomposition, chemical change due to reaction with substances from the packaging or photochemical destruction.

Stability of RMs

The following results from investigations carried out on metal ion standard solutions for atomic spectroscopy, illustrate the importance of stability tests. We tested CRMs according to ISO and commercial RMs with and without any certificate produced by various manufacturers.

Packaged standard solutions were stored at 30°C and weighed weekly. Every half-year a packet of analyte was opened and its contents tested. Figure 1 shows the mass loss of aqueous standard

solutions in glass, high density polyethylene (PE-HD) and polyvinylidene fluoride (PVDF) as a function of time. The greatest mass loss was observed for a multi-element standard in PVDF at a loss of 0.12% per month. Standard solutions in PE-HD showed a loss of 0.03% per month while at the same time the losses in glass containers were negligible. The different behaviour of the two organic packaging materials is also indicated by the different water vapour transmission rates. The transmission rate of PVDF films is considerably higher than that of equally thick PE-HD foils [3]. As expected, the danger of the RM coming concentrated due to water vapour losses through the original closed container is lowest when glass is used, but only if the cover is sufficiently tight.

Losses with the PVDF container are more critical, especially when the certified content is quoted with a relative uncertainty of around 1% and the validity of the certificate is 3 years. Under normal laboratory conditions in a warm climate, the concentration of the RM can deviate outside the certified range within a few months owing to losses caused by water vapour diffusion. The use of PVDF containers can be recommended especially for very low concentrations if interactions with the container wall such as the adsorption of analytes or leaching of foreign substances are avoided. In such cases the possible concentration of the solution must be taken into account in the quoted uncertainty. Another possibility is to specify that the container has to be stored under cool conditions. According to ISO Guide 31 the instructions for using CRMs have to specify the temperature conditions at which the container should be opened in order to prevent condensation from water vapour entering the solution when the container is opened.

Fig. 1 Weight losses of originally bottled reference material (RM) at 30°C. The percentage refers to the net weight: - - 50 ml standard solutions in pyrex-glass with screw cap, — 50 ml standard solutions in polyethylene bottles (PE-HD), — 100 ml standard solution in polyvinylidene fluoride bottles (PVDF)

It is generally known that aqueous solutions of Hg(II) are less stable. In the trace range, for instance, iodide or chloride is added for stabilisation. For RMs the measures are limited to a higher concentration of nitric acid, or possibly the addition of hydrochloric acid. Other stabilising reagents are not desirable because they can disturb individual analytical procedures. The question is: is this type of stabilised RM sufficiently stable? Based on measurements carried out on certified standard solutions with around 1000 mg/l Hg(II) in 0.1 M HNO₃ this is in fact the case if glass containers are used. After the CRM had been stored for a period of 9 months at 30 °C, we still found the same contents within the measurement uncertainty of the procedures used. When checking Hg(II) solutions from various manufacturers with concentrations of 1000 and 10 000 mg/l kept in PE containers, we determined repeated losses of mercury even though an upgrading of the solution was to be expected because of water vapour diffusion through the packaging. We plan to investigate this problem within the framework of another project.

Conclusions

In practice RMs are often the only available tool with which chemical analytical data can be traced to the SI. It is therefore important that the declared amount of substance in RMs is correct. This is only guaranteed, when the content has been correctly determined and when the stability of the substance in the original sales packaging is also included in the uncertainty estimation.

Our experience gained from the investigation and certification of RMs indicates that the measurement uncertainties quoted on commercially available standard solutions are often too small for atomic spectroscopy. In this case the overall uncertainty of a procedure could be underestimated leading to a false interpretation of the results. It is of vital importance that the uncertainty of a RM is correctly estimated and quoted, even if the relative values are clearly above 1%. In any case, for most analytical procedures RMs with a relative uncertainty of 3–5% ensure a sufficient level of quality. RMs used for the production of reference solutions must have a correctly determined uncertainty rather than one that is simply low.

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The potential of TXRF as a primary method in chemical metrology

Introduction

In the ongoing and still topical discussion being conducted by the scientific community on "primary methods of measurement in chemical analysis" [1], gravimetry, titrimetry, coulometry and isotope dilution mass spectrometry are favoured methods in terms of their potential to be primary methods.

In the context of this current discussion two points are important for analytical chemists. One is that generalists, often physicists, have taken the initiative in telling analytical chemists which of their methods are primary without regard for the chemical problems which arise as a result of homogeneity, stoichiometry, purity and matrix effects etc.

Secondly, it is somewhat surprising that neither instrumental neutron activation analysis (INAA) nor total reflection X-ray fluorescence analysis (TXRF) have been included in the discussion. The aim of this note is to demonstrate the poten-

tial of TXRF as a primary method with the aid of an example involving the quantification of Ni contamination on silicon wafers.

Example

Generally speaking TXRF is calibrated only by measuring the fluorescence radiation of a pure Ni surface as a function of the angle of incidence of the primary radiation. If the instrument used is working correctly, the measured values agree with X-ray intensities predicted by Fresnel theory within statistical uncertainties, except for a scaling factor K .

Using the Fresnel function F_∞ for a smooth, plane metal surface of sufficient thickness the resulting measured fluorescence intensity I_∞ for any instrument is

$$I_\infty = K F_\infty(\varphi, \rho, E) \quad (1)$$

where φ is the angle of incidence (the angle between the primary X-ray beam and the surface), ρ is the density of the metal and E is the energy of the primary beam.

E is known from the X-ray tube anode (e.g. Mo-K α) and φ is a known instrumental parameter which can also be determined together with K using the iterative procedure illustrated in Fig. 1.

The expression for F_∞ , which is based on classical electrodynamics, is given in Appendix 1. F_∞ contains only natural constants and no interpretable or uncertain parameters.

The factor K comprises all the quantities which depend on the properties of